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LLNL-JRNL-405947

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August 4, 2008

Journal of Computational Physics

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# Subspace Accelerated Inexact Newton method for large scale wave functions calculations in Density Functional Theory

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**Abstract**

We describe an iterative algorithm to solve electronic structure problems in Density Functional Theory. The approach is presented as a Subspace Accelerated Inexact Newton (SAIN) solver for the non-linear Kohn-Sham equations. It is related to a class of iterative algorithms known as RMM-DIIS in the electronic structure community. The method is illustrated with examples of real applications using a finite difference discretization and multigrid preconditioning.

*Key words:* Inexact Newton Iteration, Density Functional Theory, Kohn-Sham equations
*PACS:* 71.15.-m, 71.15.Dx

## 1 Introduction

Fast iterative solvers for the Kohn-Sham (KS) equations are crucial to enable large-scale first-principles simulations. It is particularly important for Born-Oppenheimer molecular dynamics simulations where the electronic ground state needs to be calculated numerous times with a relatively high accuracy. Numerous algorithms have been proposed in the physics and chemistry literature. All have their strengths and weaknesses. There is probably not one algorithm that would win in all situation, but more likely a list of good algorithms to be applied preferably according to the context: numerical basis set, code implementation and parallelization, type of application. This paper focuses on iterative algorithms for KS equations discretized on a real-space mesh

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by Finite Differences (FD) or Finite Elements (FE), or other general numerical method such as pseudo-spectral — usually referred to as Plane Waves (PW) in the electronic structure community. Atomic potentials are replaced by smoother functions using non-local pseudopotential approximations which also include the core electrons not directly involved in chemical bonds. From a mathematical point of view, such discretizations result in large sparse matrices, and lead to the use of matrix-free implementations of nonlinear iterative solvers.

The aim of this paper is to describe and analyze an iterative algorithm first introduced in the context of linear scaling methods with FD discretization [7], and later used in the context of a finite elements discretization[8]. The algorithm is presented from the point of view of a Subspace Accelerated Inexact Newton (SAIN) method, inspired by Fokkema et al [10]. Inexact Newton iterations make use of a geometric multigrid preconditioner for real-space discretization. The acceleration scheme introduced by Anderson [1] is used to accelerate convergence of the Newton iteration.

During the analysis, it became clear that this algorithm is closely related to the RMM-DIIS method as described in [14]. One major difference is the *block* or *all-bands* approach used here: all the electronic wave functions are updated simultaneously, using a single extrapolation step. The possibility of formulating DIIS as an accelerated inexact Newton scheme was pointed out by Harrison in Ref. [11].

A short review of extrapolation schemes in electronic structure calculations is given in Section 2. In Section 3, notations and formulation of the Kohn-Sham (KS) equations are introduced. Then the inexact Newton iteration method is described in section 4 before applying it to the KS equations in Section 5. More details and practical implementation of the algorithms are presented in Section 6. The numerical examples used to illustrate the algorithm in Section 7 show that the algorithm can be applied very efficiently to solve for large scale problems requiring the computations of over a thousand eigenvalues.

## 2 Extrapolation schemes in electronic structure calculations

The idea of using an extrapolation scheme to accelerate convergence of a Newton iteration in electronic structure calculations goes back to Pulay [18] in 1980. He gave the name DIIS for *Direct Inversion of the Iterative Subspace* to his approach. Related algorithms are also found under the name "Pulay mixing". While Pulay described his original approach for extrapolating a Fock matrix based solution of a self-consistent calculation — represented in a space spanned by a set of local atomic orbitals — the name DIIS was later used in

the community for various extrapolation based algorithms.

In this paper, the focus is on using a similar extrapolation scheme to calculate directly the wave functions solutions of the Kohn-Sham (KS) equations. For this purpose, Wood and Zunger [21] described an algorithm they call "RMM-DIIS", attributed to Bendt and Zunger. This algorithm uses the DIIS extrapolation scheme to minimize the residual of an eigenvalue problem associated to a targeted eigenpair. Alternative implementations for DFT calculations using a Gaussian basis set [9] or Plane Waves [14] were proposed later. Hutter et al. [12] proposed another adaptation of DIIS for optimizing the Kohn-Sham eigenstates in plane waves using the extrapolation scheme to minimize the preconditioned residuals.

DIIS extrapolation coefficients at step $k$ of the iterative process are determined by requiring that the 2-norm of an extrapolated error vector $\bar{e}_k$, made of a linear combination of the estimated current error $e_k$ and the estimated errors at the previous $m$ steps,

$$\bar{e}_k = \sum_{i=0}^{m} c_i e_{k-i},$$

is minimized under the constraint

$$\sum_{i=0}^{m} c_i = 1. \tag{1}$$

This leads to a system of $m+2$ linear equations for the $m+1$ coefficients $c_i$ and the Lagrange parameter associated with the constraint.

A similar extrapolation scheme had been proposed earlier by D.G. Anderson [1] for solving more general nonlinear equations. Anderson writes

$$\bar{e}_k = e_k + \sum_{1=1}^{m} \theta_i (e_{k-i} - e_k).$$

The latter equation can also be written as

$$\bar{e}_k = (1 - \sum_{1=1}^{m} \theta_i) e_k + \sum_{1=1}^{m} \theta_i e_{k-i}.$$

Thus, the equivalent DIIS coefficients are given by

$$\begin{aligned} c_i &= \theta_i, i = 1, \ldots, m \\ c_0 &= 1 - \sum_{1=1}^{m} \theta_i \end{aligned}$$

and clearly satisfy the constraint (1).

The particular choice of the error function varies depending on the specific quantity one tries to minimizes: residual of eigenvalue problem, computed iterative correction, electronic density self-consistent updates, even atomic forces in geometry optimizations.

Extrapolation written under the "Anderson" form was also used in the electronic structure community, for instance to accelerate self-consistent iterations by extrapolating potentials obtained at successive iterations[15]. Similar schemes to mix the density between self-consistent iterations are also common under the name "Pulay mixing". The Anderson extrapolation scheme was recently used by the author and others [7,8] to optimize subspaces associated to DFT orbitals represented in a general nonorthogonal representations.

## 3 Density Functional Theory

We consider the DFT energy functional written as a functional of $N$ orthonormal electronic wave functions $\psi_i$ (KS model)

$$\begin{aligned} E_{KS}[\{\psi_i\}_{i=1}^N] = & \sum_{i=1}^N \int_\Omega \psi_i(r) \left(-\triangle \psi_i\right)(r) dr \\ & + \frac{1}{2} \int_\Omega \int_\Omega \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + E_{XC}[\rho] \\ & + \sum_{i=1}^N \int_\Omega \psi_i(r) (V_{ext}\psi_i)(r) dr. \end{aligned} \tag{2}$$

where $\rho$ is the electronic density defined by

$$\rho(r) = \sum_{i=1}^N |\psi_i(r)|^2 \tag{3}$$

(see for example [3]). $E_{KS}$ is made of the sum of the kinetic energy of the electrons, the Coulomb interaction between electrons, the exchange and correlation electronic energy, and the energy of interaction of the electrons with the potential generated by all the atomic cores $V_{ext}$. Given an external potential $V_{ext}$ — defined by the various atomic species present in the problem, their respective positions and pseudopotentials — the ground state of the physical system is obtained by minimizing the energy functional (2) under the orthonormality constraints

$$\int_\Omega \psi_i(r)\psi_j(r) = \delta_{ij}, i, j = 1, \ldots, N. \tag{4}$$

To avoid mathematical difficulties irrelevant to the present study, let assume from here on that we have to solve a problem in a finite dimensional space of dimension $M$ resulting from the discretization of the above equations. To be concrete, suppose we have a finite difference discretization on a uniform mesh with periodic boundary conditions, and thus the functions $\psi_i$ are M-dimensional vectors with components corresponding to their values at the mesh points, $\psi_{i,k} = \psi_i(r_k)$. Let denote by $L_h$ the finite difference approximation of the Laplacian operator.

One can derive the Euler-Lagrange equations associated to the minimization problem (2) with $N^2$ Lagrange parameters corresponding to the orthonormality constraints (4). One obtains the so-called Kohn-Sham equations in their usual form for the particular choice of the functions $\{\psi_i\}_{i=1}^N$ which diagonalizes the matrix $\Lambda$ made of the Lagrange parameters, $\Lambda_{ij} = \lambda_i \delta_{ij}$

$$\begin{aligned} -L_h\psi_i + V_{KS}[\rho]\psi_i &= \lambda_i\psi_i \\ \rho(r_k) &= \sum_{i=1}^{N} |\psi_i(r_k)|^2 \\ \sum_{k=1}^{M} \psi_i(r_k)\psi_j(r_k) &= \delta_{ij} \end{aligned} \tag{5}$$

where $V_{KS}$ is a discretized nonlinear effective potential operator (see *e.g.* [3]). In this approach, one has to find the $N$ lowest eigenvalues $\lambda_i, i = 1, \ldots, N$ and the corresponding eigenfunctions. We assume here that $\lambda_{N+1} - \lambda_N > 0$.

Let $V$ denote the set of matrices of $M$ rows and $N$ columns. We can represent the solution of the discretized problem as a matrix

$$\Psi = (\psi_1, \ldots, \psi_N) \in V \tag{6}$$

$\Psi$ represents the invariant subspace spanned by the eigenvectors associate to the $N$ lowest eigenvalues. Using these notations, the KS equations are given by

$$-L_h\Psi + V_{KS}[\rho]\Psi = \Psi\Lambda \tag{7}$$

where $\Lambda = diag(\lambda_1, \ldots, \lambda_N)$ is a diagonal matrix with diagonal entries $\Lambda_{ii} = \lambda_i$.

We define

$$H_h[\rho] = -L_h + V_{KS}[\rho]. \tag{8}$$

Let's assume we have another representation of that same subspace by $N$ linearly independent vectors,

$$\Phi = (\phi_1, \ldots, \phi_N) \in V \tag{9}$$

One can find an $N \times N$ matrix $C$ such that

$$\Psi = \Phi C. \tag{10}$$

The matrix $C$ satisfies

$$CC^T = S^{-1} \tag{11}$$

where $S = \Phi^T \Phi$, the Gram matrix, is of rank $N$. Using relations (10) and (11), one can express the electronic density in terms of the matrix elements of $\Phi$ and $S^{-1}$,

$$\rho_k = \sum_{i,j=1}^{N} \left(S^{-1}\right)_{ij} \Phi_{ki} \Phi_{kj} \tag{12}$$

where $\rho_k$ denotes the value of the electronic density at the mesh point $x_k$. Also the KS equations for $\Phi$ can be rewritten as

$$-L_h \Phi + V_{KS}[\rho]\Phi = \Phi S^{-1} H_\Phi \tag{13}$$

where $H_\Phi = \Phi^T(-L_h + V_{KS})\Phi$. For a trial solution $\Phi$, the residual is given by

$$R(\Phi) = -L_h \Phi + V_{KS}[\rho]\Phi - \Phi S^{-1} H_\Phi \tag{14}$$

It is easy to verify that

$$\Phi^T R(\Phi) = 0.$$

Beside the fact that one has to be careful in avoiding cases where the columns of $\Phi$ become degenerate, this is now an unconstraint nonlinear problem. Such a formulation is convenient to implement acceleration algorithms like the one described later in this paper. It has also been used for conjugate gradient algorithm implementation in electronic structure calculations [20].

We define the following dot product between 2 elements of $V$ as

$$(\Phi_1, \Phi_2)_V = Tr(C_1^T \Phi_1^T \Phi_2 C_2) = Tr(C_2 C_1^T \Phi_1^T \Phi_2) \tag{15}$$

where $C_i$ is a linear transformation that maps $\Phi_i$ into a matrix made of orthonormal vectors. It has the important property of being independent of the particular representation $\Phi$ chosen for a given subspace. If $\Phi_1 = \Phi_2 = \Phi$,

$$(\Phi, \Phi)_V = Tr(S^{-1} \Phi^T \Phi) \tag{16}$$

leading to the definition

$$(\Phi_1, \Phi_2)_S := Tr(S^{-1} \Phi_1^T \Phi_2). \tag{17}$$

## 4 Inexact Newton

We consider the general nonlinear equation

$$F(u) = 0 \tag{18}$$

where $F$ is some smooth nonlinear functional defined in a finite dimensional space $\mathcal{V} \in R^n$, where n is typically very large. One type of such equations is

$$A(u) = \lambda(u)u \tag{19}$$

with $\lambda(u) = (u, Au)/(u, u)$, and A is a nonlinear operator. The nonlinearity of A, which typically appears in Density Functional Theory, is one of the particular features which leads to not rely on standard eigensolvers for an efficient solution of this problem.

Newton's method is a well known iterative approach to solve nonlinear equations such as (18) (see *e.g.* [17]). One basic iterative step to improve an approximate solution $u_k$ at step $k$ can be written as

$$u_{k+1} = u_k - J_k^{-1} F(u_k) \tag{20}$$

where $J_k := F'(u_k)$. Thus we can write a linear equation for the correction $p$ of $u_k$,

$$J_k p_k = -r_k \tag{21}$$

where $r_k = F(u_k)$. Unfortunately, the Jacobian $J_k$ is often not available or practically impossible to compute. It can also be computationally very expensive or impossible to solve exactly the linear system (21). For large $n$, it is more practical to use an approximate Jacobian $\tilde{J}_k$, leading to an inexact Newton iteration [5]

$$u_{k+1} = u_k - \tilde{J}_k^{-1} F(u_k) \tag{22}$$

The inexact correction equation can then also be solved approximately, by an iterative method such as multigrid for example. Note that even if Eq. (21) is solvable, searching for an accurate solution may not be efficient if the quadratic model used to derive the Newton equation differ significantly from the real behavior of $F(u)$.

If we are in a quadratic regime close to a solution $\bar{u}$, where

$$r_k = J_k(u_k - \bar{u}),$$

we have, using (22),

$$u_{k+1} = \bar{u} + (I - \tilde{J}_k^{-1} J_k)(u_k - \bar{u}) \tag{23}$$

This simple iterative process converges if the eigenvalues of the matrix $(I - \tilde{J}_k^{-1} J_k)$ are of modulus smaller than 1. The convergence rate obviously depends

on the largest eigenvalues of $(I-\tilde{J}_k^{-1}J_k)$ and thus on how well $\tilde{J}_k$ approximates $J_k$. Note that for an eigenvector search, since the solution is defined up to multiplicative factor, one should really consider the operator [19]

$$(I - u_k u_k^T)(1 - \tilde{J}_k^{-1}J_k)(I - u_k u_k^T).$$

## 5 Accelerated Inexact Newton for KS

The nonlinear KS problem to solve for can be written as

$$F(u) = R(\Phi) = -L_h\Phi + V_{KS}[\rho]\Phi - \Phi S^{-1}H_\Phi = 0 \tag{24}$$

and the corresponding inexact Newton iteration

$$\Phi_{k+1} = \Phi_k - \tilde{J}_k^{-1}R(\Phi_k). \tag{25}$$

Let

$$P_k = -\tilde{J}_k^{-1}R(\Phi_k), \tag{26}$$

denote the subspace correction computed at step $k$.

The simplest approximate Jacobian $\tilde{J}_k$ one could use is the identity scale by a factor

$$\tilde{J}_k = \eta I.$$

In the language of eigensolvers, it leads to a block shifted power method (see *e.g.*[2], section 11.3). It is also called gradient method for computing the smallest eigenvalue since $R$ is colinear to the gradient of the Rayleigh quotient. Such an approach can be substantially improved if a good preconditioner $T$ is available by choosing

$$\tilde{J}_k = T.$$

Iteration (25) then becomes a subspace preconditioned inverse iteration. For a linear positive definite operator $A$, Neymeyr [16] demonstrated its convergence to the invariant subspace spanned by the eigenvectors associated to the lowest $N$ eigenvalues of $A$. The main assumptions are that $\lambda_{N+1} > \lambda_N$ and $T$ is a good approximation of $A$ in the sense that

$$\|I - TA\|_A \leq \gamma$$

for $\gamma \in (0, 1)$. In practice, due to numerical rounding errors, this iteration converges for initial subspaces generated from scratch. For an appropriate choice of the preconditioner, this algorithm leads to a mesh independent convergence rate with a very small cost iteration. For KS equations discretized on a mesh or in Plane Waves, a good option is to use a preconditioner $T$ which approximates $(-L_h)^{-1}$. Here we use the multigrid preconditioner proposed in [6].

Newton's method is a one-step method which uses information only from the current step to improve a trial solution. To accelerate convergence however, one can use information accumulated during the previous $m$ steps, to build an improved trial solution. Such an approach is referred to as an Accelerated Inexact Newton (AIN) method [10]. Instead of simply adding the correction $P_k$ to the current approximation $\Phi_k$, the idea is to use the knowledge accumulated during the $m$ previous Newton steps to build a better update. Let

$$V_{k,m} := [\Phi_{k-m}, P_{k-m}, \ldots, \Phi_k, P_k] \tag{27}$$

be a search space. An improved update for $\Phi_k$ would be

$$\bar{\Phi}_k = V_{k,m} y \tag{28}$$

where $y \in R^{(2m+2)N}$ is solution of a projected problem in $V_{k,m}$.

Fokkema et al. [10] proposed various conditions (projected problems in appropriately chosen search subspace) to determine the vector of coefficients $y$: a Galerkin condition, a minimum residual condition, or a mix of both. In the Davidson-Liu algorithm [4] for instance, one would solve a Galerkin problem in the space

$$V_{k,DL} = [\Phi_k, P_k].$$

In LOBPCG [13], one would solve instead a Galerkin problem in the space

$$V_{k,LOBPCG} = [\Phi_{k-1}, \Phi_k, P_k]$$

to get the optimal solution within this subspace. However an optimal algorithm has to take into account some of the features specific to DFT calculations: a nonlinear operator and a large number of eigenpairs to compute. Yang et al.[22] proposed to generalize LOBPCG and solve iteratively a nonlinear $3N \times 3N$ problem in $V_{k,LOBPCG}$. This is a very robust approach. However building multiple times $3N \times 3N$ matrices, with elements made of dot products between pairs of M-dimensional vectors, becomes quite costly for large scale problems.

Here we use a much less computationally demanding method based on minimizing an extrapolated residual. In Ref. [1], Anderson proposed an extrapolation based on the solution of a projected linear problem defined by the residuals computed at the $m$ previous steps. It can be regarded as a linearized minimum residual condition

$$min_{y \in \Re^{m+1}, \|y\|=1} \| \sum_{j=0}^{m} y_j R(\Phi_{k-j}) \|,$$

a block variant of RMM-DIIS. The basic idea is to write an extrapolation

scheme for $\Phi$, using the approximations at the previous $m$ steps,

$$\bar{\Phi}_k := \Phi_k + \sum_{j=1}^{m} \theta_j (\Phi_{k-j} - \Phi_k). \tag{29}$$

Assuming a quadratic regime, the same extrapolation scheme holds for $R$, and thus for $P$,

$$\bar{P}_k := P_k + \sum_{j=1}^{m} \theta_j (P_{k-j} - P_k). \tag{30}$$

The real coefficients $\theta_j$ are defined as those which minimize the norm of $\bar{P}_k$. They can be found by solving the $m \times m$ linear system defined by

$$\sum_{j=1}^{m} (P_k - P_{k-i}, P_k - P_{k-j})_S \theta_j = (P_k - P_{k-i}, P_k)_S, \qquad i = 1, \ldots, m. \tag{31}$$

Finally, the new trial solution in $V_{k,m}$ is computed as

$$\Phi_{k+1} = \bar{\Phi}_k + \beta \bar{P}_k.$$

where the parameter $\beta$ is usually chosen to be 1.

Note that the equations for the coefficients $\theta_j$ are very similar to those obtained by Harrison [11] for his Krylov Subspace accelerated inexact Newton (KAIN) method. They differ by the choice of the left projector used to define the projected system (31).

## 6 Practical Implementation

The evaluation of the dot product $(.,.)_S$ defined in (17) becomes quite expensive for large $N$ since it involves $N^2$ dot products between vectors of length $M$. In practice the approximation

$$Tr(\bar{P}^T \bar{P} S^{-1}) \sim \sum_{i=1}^{N} \bar{P}_i^T \bar{P}_i (S^{-1})_{ii}.$$

is used. It requires only $O(N)$ dots products. (Here $\bar{P}_i$ denotes the column $i$ of $\bar{P}$.) This approximation becomes exact for orthogonal vectors. If vectors are orthogonalized at regular intervals, for instance once at every ionic positions update in a molecular dynamics, this approximation remains very good.

Since the SAIN algorithm makes use of a residual minimization for an eigenvalue problem, there is a risk to converge to interior eigenvalues since the

residual of an eigenvalue problem is zero for any eigenpair. To remedy this issue, extrapolation is turned off if the trial solution is too far away from convergence. This reduces SAIN to a subspace preconditioned inverse iteration in the initial steps when no good trial solution is known.

Another common issue observed in electronic structure problems solving with SAIN is the local non-convexity of the energy surface. In that case minimizing the residual would lead towards an energy maximum. Such a problem can be detected by looking at the extrapolation coefficients $\theta_j$. Let us consider for example the case $m = 1$ and assume the energy functional follows a quadratic function between $\Phi_{k-1}$ and $\Phi_k$, with $E[\Phi_k] < E[\Phi_{k-1}]$. Then a proper extrapolation with a convex energy functional should lead to $\theta < 0.5$. This suggests one should discard coefficients larger than 0.5. For coefficients larger than 1, we actually assume local concavity and use an extrapolation with $\theta = -0.5$. We also treat with precautions coefficients smaller than $-3$ corresponding to very large extrapolation.

The complete procedure is detailed in Algorithm 1. One notices in particular that SAIN can be implemented with only one full Hamiltonian matrix application per Newton iteration and per wave function. Other costly operations for large systems include building the matrices $S$ and $H_\Phi$, and potentially applying the preconditioner $T$.

## 7 Numerical results

As a first illustration, let us consider a simple eigenvalue problem

$$Au = \lambda u$$

where $A$ is a real symmetric $M \times M$ matrix. Without loss of generality, we can assume $A$ diagonal. Suppose the diagonal elements of $A$ are given by $a_{ii} = \lambda_i = i$ for $i = 0, \ldots, M-1$. Let us consider the problem of finding the lowest eigenvalue $\lambda_0 = 0$ and the associated eigenvector $u_0 = (1, 0, \ldots, 0)^T$. We start with an initial guess given by $\tilde{u}_0 = (0.447, 0.894, 0., \ldots, 0)^T$, that is with non-zero components along the eigenvectors corresponding to the lowest 2 eigenvalues.

Let $M = 10$ and set $m = 1, T = 1/\lambda_{max} \cdot I$ where $\lambda_{max}$ is the largest eigenvalue of $A$. For this simple problem the energy is the sum of the Ritz value associated with the current iterative solution $\tilde{u}$. It is also a measure of the error during the SAIN iterations. We plot it as a function of the angle between $\tilde{u}$ and $u_1$ — in the plane defined by $u_0$ and $u_1$. The solution is reached for an angle of $\pi/2$. Results are plotted in Fig. 1 and show how the initial iterations are not very

**Algorithm 1** Subspace Accelerated Inexact Newton (SAIN)

$k \Leftarrow 0$, $\tilde{m} \Leftarrow 0$, $V_{-1} \Leftarrow [\,]$
Set $\Phi_0$ to initial guess
Compute $S = \Phi_0^T \Phi_0$, $\rho_0$, $V[\rho_0]$ and $H_\Phi = \Phi_0^T H_0 \Phi_0$
$R_0 \Leftarrow H_k \Phi_0 - \Phi_0 S^{-1} H_\Phi$
**repeat**
  $P_k \Leftarrow -T R_k$
  $V_k \Leftarrow [V_{k-1}, \Phi_k, P_k]$
  $flag \Leftarrow true$
  **while** flag *and* $\tilde{m} > 0$ **do**
    $flag \Leftarrow false$
    **if** $dim(span(V_k)) > 2(\tilde{m}+1)N$ **then**
      remove left $2N$ columns of $V_k$
    **end if**
    Build linear system (31)
    **if** cond(linear system) $< 100$ **then**
      Solve linear system (31) to determine $\theta_j, j = 1, \ldots, \tilde{m}$
      **if** $max_j(\theta_j) > 0.5$ *or* $min_j(\theta_j) < -3$ **then**
        **if** $\tilde{m} > 1$ **then**
          $\tilde{m} \Leftarrow \tilde{m} - 1$, $flag \Leftarrow true$ {Reduce history length}
        **else**
          **if** $\theta_1 > 1$ **then**
            $\theta_1 \Leftarrow -0.5$ {Fixed extrapolation for concave regime}
          **end if**
          $\theta_1 \Leftarrow min(max(\theta_1, -3), 0.)$ {Limit extrapolation}
        **end if**
      **end if**
    **else**
      $\tilde{m} \Leftarrow \tilde{m} - 1$, $flag \Leftarrow true$ {Reduce history length}
    **end if**
  **end while**
  $y \in R^{2(\tilde{m}+1)N}$
  **for** $i = 1$ to $N$ **do**
    $y(i) = 1 - \sum_{j=1}^{\tilde{m}} \theta_j, \quad y(i+N) = \beta y(i)$
  **end for**
  **for** $j = 1$ to $\tilde{m}$ **do**
    **for** $i = 2jN + 1$ to $2jN + N$ **do**
      $y(i) = \theta_j, \quad y(i+N) = \beta y(i)$
    **end for**
  **end for**
  $\Phi_{k+1} \Leftarrow V_k y$
  $k \Leftarrow k + 1$
  Update $S = \Phi_k^T \Phi_k$, $\rho_k$, $V[\rho_k]$ and $H_\Phi = \Phi_k^T H_k \Phi_k$
  $R_k \Leftarrow H_k \Phi_k - \Phi_k S^{-1} H_\Phi$
**until** $\|R_k\| < tol$

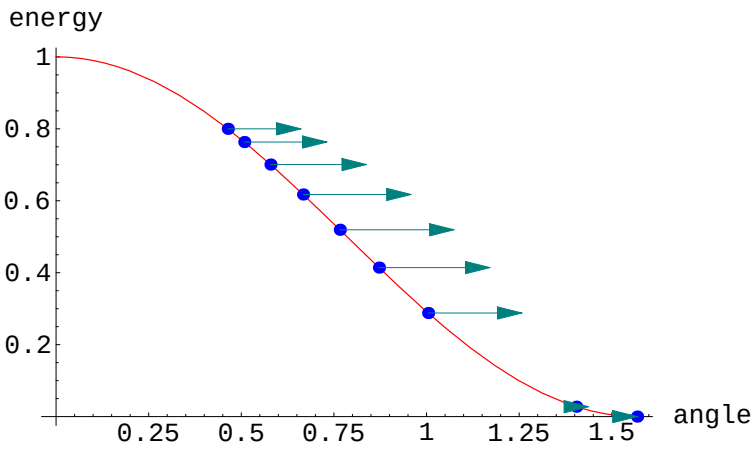


Fig. 1. Convergence of SAIN algorithm for search of lowest eigenvalue of of matrix $A$ (see text). Arrows denote magnitude of gradient at each trial solution. No acceleration is performed until the convex region is reached.

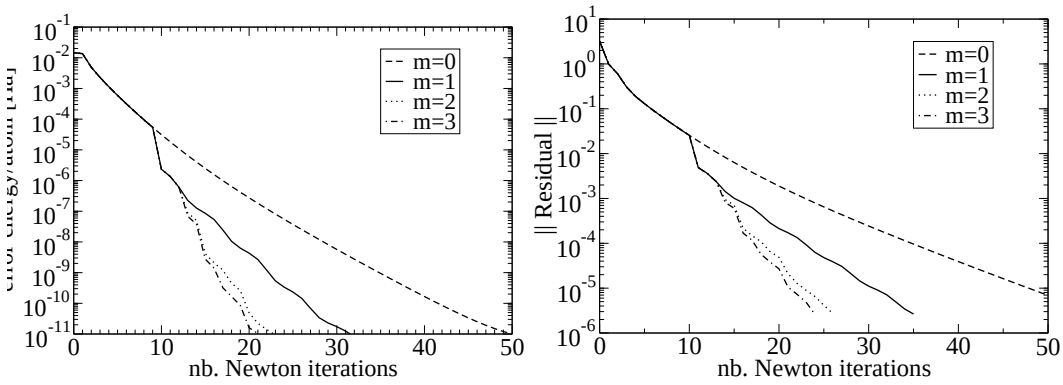


Fig. 2. Convergence of energy and residual for $Si_{35}H_{36}$ cluster for various history length ($m$).

efficient since the preconditioner is not very good and the trial solution is in a concave regime. But as soon as the convex regime is reached, acceleration quickly leads to the solution.

Now switching to real application, the next test consists in calculating the ground state of a silicon cluster passivated with H atoms at the surface ($Si_{35}H_{36}$). Like al the other applications presented in this paper, the Local Density Approximation (LDA) exchange and correlation functional was used together with norm-conserving pseudopotentials. The convergence rate for the total energy and the residual defined by Eq. (24) is shown in Fig. 2 using SAIN with various history lengths $m$. The case $m = 0$ corresponds to a subspace preconditioned inverse iteration with no acceleration. The initial trial wave functions used here are Gaussians functions centered on atomic bonds. The numerical results show that the effect of acceleration is quite important for $m = 1$ and $m = 2$. Going beyond $m = 2$ does not help much.

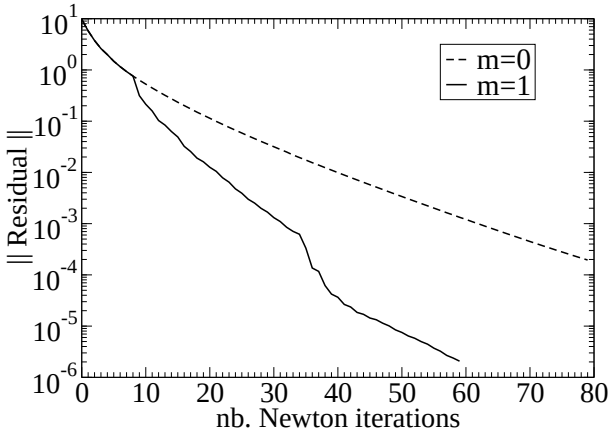


Fig. 3. Convergence for $Si_{512}$ crystal (N=1024).

To illustrate the applicability of the algorithm described in this paper to really large problems, we consider the calculation of the electronic structure of a silicon crystal of 512 atoms. In a typical pseudopotential DFT calculation for this system, one has to compute 1024 wave functions. The problem is discretized on a uniform $64 \times 64 \times 64$ mesh. Wave functions were initialized as Gaussian functions centered on bonds. Convergence of SAIN is shown in Fig. 3.

Problems involving dangling bonds are typically more difficult to solve than the two previous examples — with fully saturated bonds — and iterative algorithms usually converge slower towards the ground state. To illustrate the efficiency of the SAIN algorithm on such problems, it is applied to the ground state calculation of a diamond C(100) surface. A slab made of 12 layers of C atoms was used, with one surface terminated by a layer of H atoms to passivate the dangling bonds and the other surface reconstructed, as proposed for instance in [23]. The unit cell was repeated 4 times along each of the 2 axis parallel to the surface, making it a 416 atoms system, with 784 electronic wave functions to compute. Fig. 4 shows the convergence of the SAIN algorithm for a $2 \times 1$ reconstructed surface. Compared to the two previous examples, a slower but quite good convergence rate is observed.

In practical applications, the electronic structure ground state often needs to be computed many times for slightly different atomic configurations. This is the case for molecular dynamics (MD) simulations or geometry optimizations where the electronic structure is used to evaluate forces acting on atoms at each step of the atomic configuration trajectory. In that case the initial trial wave functions are provided by the solution computed at the previous step or an extrapolation using a few additional previous steps. The problem then becomes to quickly reach the new ground state for a slightly different Hamiltonian. The performance of SAIN in this situation is illustrated in Fig. 5. It shows the convergence of the residual for 5 consecutive steps of molecular dynamics of

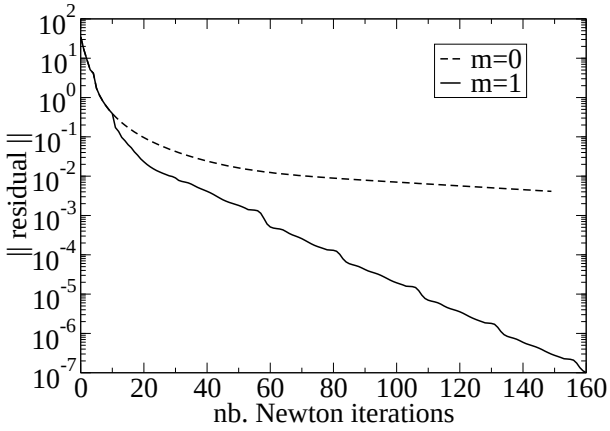


Fig. 4. SAIN (N=784).

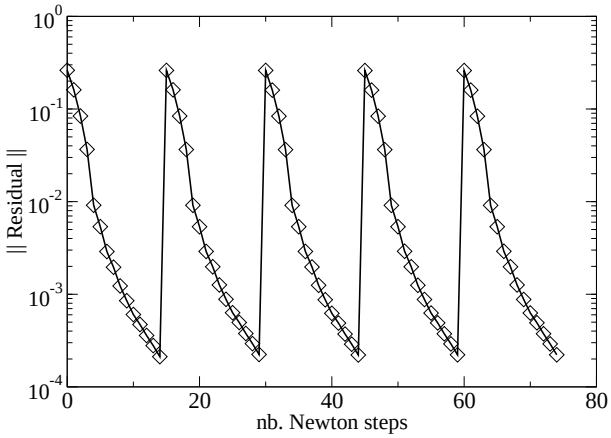


Fig. 5. SAIN convergence for $H_2O$ molecular dynamics with 64 molecules (N=256).

liquid water at ambient conditions (64 molecules cell). At each MD step, wave functions are initialized with an initial guess given by

$$\tilde{\Phi}_k = 2\Phi_{k-1} - \Phi_{k-2}.$$

For the iterations shown in Fig. 5, $m = 1$ and Anderson extrapolation is performed at every step except for the first step after updating atomic positions. The jumps in residual correspond to atomic configurations updates.

## 8 Concluding Remarks

As seen from the numerical results presented in the previous section, small values of $m$ are usually appropriate for the SAIN algorithm. The optimal value for $m$ depends on the preconditioner $T$, but $m = 1$ or $m = 2$ are often good values. Using larger values often results in bad conditioning for the linear

system (31) and $m$ being cut automatically (see Algorithm 1).

A major assumption for the SAIN algorithm to work well is to have a band gap in the eigenvalues spectrum, $\lambda_N < \lambda_{N+1}$. If $\lambda_N$ is degenerate or nearly degenerate, extrapolation is not valid anymore for residuals corresponding to Ritz vectors associated to the eigenvalues close to $\lambda_N$. One way to remedy this issue is to replace $S^{-1}$ by the single particle density matrix in the definition of the dot product $(.,.)_S$ (Eq. 17) in order to progressively decrease the weigh of the contributions coming from those Ritz vectors. Further study is needed for this problem.

As mentioned in the introduction, an interesting aspect of the algorithm presented here is its direct applicability in the linear scaling context, when electronic wave functions are confined to limited regions in space[7]. It is in particular due to the fact that no Rayleigh-Ritz procedure is required in SAIN. For localized electronic wave functions, the only adaptation needed is to replace the orthonormalization procedure by a simple normalization of all the wave functions.

## 9 Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Financial support from US Department of Energy/SciDAC project on Quantum Simulation of Materials and Nanostructures is gratefully acknowledged.

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